SEPARATION OF RARE EARTHS BY MIXTURES OF AN IONIC LIQUID AND A NEUTRAL EXTRACTANT

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The European Union defined the rare-earth elements (REEs) as critical metals due to their high economic value (increasing demand in motors, electronics, renewal energy and catalysts) and high supply risks (>95% sourced from China).[1] The most important process for separating mixtures of REEs is the solvent extraction (SX). In SX, a pregnant leach solution (PLS) derived from the dissolution of a material enriched in REEs, is intensively mixed with an immiscible organic phase. After phase disengagement, the organic phase selectively extracts the desired element(s). Then, the process is reversed by contacting the loaded organic phase with a strip solution, in order to recuperate the element(s) of interest and recycle the organic phase for next SX processes. Extraction can be carried out from a HCl or a HNO_3 solution. Using HCl is cheaper than HNO_3, but the chloride route requires the use of acidic extractants which implies difficult stripping, large consumption of bases for pH control and strong acids for REE stripping (higher OPEX), and there are issues with gel formation. In that regard, the preferred alternative are neutral extractants, but these cannot efficiently extract REE from chloride solutions. The present work studies the extraction of REE with a neutral extractant and from a chloride medium, using "split-anion extraction".[2]

The organic phase consisted of the neutral extractant Cyanex® 923 (a commercial mixture of four trialkyl (octyl/hexyl) phosphine oxides) diluted into the water-saturated ionic liquid Cyphos® IL-101 in its nitrate or thiocyanate form (trihexyl(tetradecyl)phosphonium nitrate/thiocyanate). The aqueous phase was a synthetic feed solution that simulates the composition of a HCl PLS originating from the Kringlerne (Greenland) REE deposit (77 g/L of REE chlorides) in a 2.5 M $CaCl_2$ matrix. Extraction processes were performed in glass vials in the millilitre scale, as a function of different parameters, and both organic and aqueous phases were monitored by total reflection X-ray fluorescence (TXRF).

Dissolving 20 v% Cyanex® 923 into the ionic liquids substantially increased the loading capacity of the organic phase (35-40 g/L) due to the strong interactions of the phosphine oxides (high Guttmann donor number), with the Lewis acidic REE-nitrate complex. Furthermore, adding Cyanex® 923 to the nitrate Cyphos® IL 101 changed the extraction across the lanthanide series from a negative to a positive sequence (i.e. La is less extracted than Lu), with Y behaving similarly to Pr-Nd. The fact that La, Ce, Pr, Nd and Y remains in the raffinate after SX is convenient because these elements make up the 77 w% of the total REE and, therefore, the organic phase and the extraction stages needed for their full separation from the rest of the heavier REE are reduced. In the case of the thiocyanate ionic liquid, heavy REE are preferentially extracted with and without Cyanex® 923. The

separation of REE can be adjusted to a desire group of the heaviest REE by varying/optimizing the volume phase ratio aqueous:organic in such a way that the loading capacity of the organic phase is equal to the concentration of the desired heaviest REE. This calculation is based on the feed concentrations and the availability of extractant and complexing anions. When the organic phase reaches its loading capacity, the heavier REE (higher distribution ratios) have a significant crowding effect on the extraction of the lighter REE (lower distribution ratios), displacing them out of the organic phase. Thus, the lower the aqueous:organic ratio is, the more different REE are being extracted. With regard to stripping, the loaded organic phases can easily be stripped with water, with >90% recovery of the previously extracted REE after one contact in 1:1 v:v ratio.

Split-anion extraction with a neutral extractant is a cost- and resource-efficient process for the recovery of REE from chloride leaching solutions of representative European REE ores. Using quaternaryphosphonium ionic liquids with nitrate or thiocyanate anions instead of molecular organic diluents (volatile, flammable and non-electrically conductive) and stripping with water instead of acids leads to safer and environmentally friendlier SX processes. Finally, the parameters necessary for upscaling to a pilot plan were calculated for the stages of extraction, stripping and regeneration. These include the flow sheet, the organic to aqueous ratios, the number of mixer-settler stages, operation temperature, mixing time, surface loading and selection of the continuous phase. This is necessary for further research on developing a system which could be considered for commercial/industrial operation.

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References

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